



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/BE88/00003 <b>(22) International Filing Date:</b> 11 February 1988 (11.02.88) <b>(31) Priority Application Number:</b> PCT/BE87/00001 <b>(32) Priority Date:</b> 13 February 1987 (13.02.87) <b>(33) Priority Country:</b> NL  <b>(71) Applicant:</b> LABOFINA S.A. [BE/BE]; 52, rue de l'Industrie, B-1040 Bruxelles (BE).  <b>(72) Inventors:</b> VAN DER KOLK, Cornelis, E., M.; Rossin-straat 118, NL-1962 EJ Heemskerk (NL). VAN DER POEL, Hendrick; Turfschip 155, NL-1186 XG Amstelveen (NL). BRAEKEN, Jozef; Lindestraat 88, B-9470 Denderleeuw (BE).		<b>(74) Common Representative:</b> LABOFINA S.A.; Siège de Feluy, Zone Industrielle C, B-6520 Feluy (BE).  <b>(81) Designated States:</b> AT (European patent), AU, BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB, GB (European patent), IT (European patent), JP, KR, LU (European patent), NL, NL (European patent), SE (European patent).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> IMPROVED SHOP PRIMER COMPOSITIONS  <b>(57) Abstract</b> <p>A shop primer composition comprising (i) fillers and pigments, at least 25 wt % of which have conductive properties; (ii) zinc powder in a weight ratio of between 1:6 to 1:1 to the fillers and pigments; said zinc, fillers and pigments being milled to a sufficient fineness; (iii) anti-settling agents; (iv) optionally, thickening agents; (v) a silicate-type binder, in an amount such that the weight ratio of the SiO<sub>2</sub> content of said binder to the zinc, fillers and pigments is of from 1:4 to 1:16; and (vi) solvents. When using this shop primer composition, the welding properties are improved and the health hazards during welding are reduced, without having to remove the primer layer at the welding area. The primer coatings are compatible with the welding techniques generally used in the heavy steel construction industry, including MIG/MAG welding in 3F position.</p>		

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### IMPROVED SHOP PRIMER COMPOSITIONS

The present invention relates to an improved composition for application as shop primer in the steel industry. More particularly, it relates to a shop primer composition for coatings which do not interfere with the welding operations or give off toxic fumes during said operations.

When bare steel is used for construction purposes, blasting and primer coating have to be carried out in situ, thereby involving higher costs. Therefore, the rolled steel is now generally blasted using automatic procedures and immediately coated with a thin shop primer coating.

The requirements for shop primers are multiple :

- they should be easily sprayable;
- they should dry fairly rapidly;
- they should provide a good, although temporary, protection against corrosion;
- the primer layer should have a good mechanical resistance;
- the primer coating should not impair the weldability;
- no health hazards should exist during welding;
- the primer coating should be compatible with the further protections used.

The most common types of welding techniques in the heavy steel construction industry are based on the generation of an electric arc between an electrode and the workpiece, the difference residing in the method used for protecting the weldpool against oxidation. The most

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important ones are :

1. Manual Metal Arc Welding (also called Shielded Metal Arc or Rod Welding) wherein the molten seam is protected by the melting of the flux provided around the rod. This welding technique is mainly used in a manual way, although automated horizontal rod welding (also called gravity welding) is known and used. Manual rod welding can be used in all welding positions, but with low welding speed. After welding, the flux remains as slag on top of the weldseam, and it must be removed before any coating operation.
2. Submerged Arc Welding (also called Under Powder Welding) : this technique is automatic and allows high welding speed, but obviously only for horizontal welds. The powder partially melts and remains on top of the weldseam; the rest is sucked away.
3. MIG/MAG welding (Metal Inert Gas/Metal Active Gas welding), wherein a flow of gas is provided around the electrode core to protect the molten seam. The gas used is pure argon (or other inert gas) in the case of MIG welding, or it can be a combination of argon (or other inert gas) with carbon dioxide (sometimes with oxygen) in the case of MAG welding. MIG/MAG welding is often preferred because it can be used with automatic welding machines in horizontal welding positions, resulting in higher welding speeds than with other welding techniques. Further, manual MIG/MAG welding with automatic electrode feeding (usually called semi-automatic welding) is also possible; in such case, the welding speed can also be higher than with other manual welding techniques. Still a further advantage of MIG/MAG welding is that the heat-affected zones are smaller than with other electric arc welding method.

When welding a T-joint, two seams are to be formed on either sides. However, when using MIG/MAG welding, the seam solidifies more rapidly. Thus, when the second seam is formed, any gas formed through combustion of

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the primer can no more escape between the parts to be welded, and is therefore likely to cause pore formation in the seam.

It is known to use shop primers based on organic binders, most frequently based on epoxy resins or on polyvinyl butyral reinforced phenolic resins. However, these binders form gases during the welding process, thereby resulting in severe internal (i.e. non visible from the outside) and external porosity of the weldseam. Also, the primer coating alongside the weldseam and on the reverse side is overheated during welding, forming what are called "burn back" zones, and the subsequent paint coatings are likely to perform less on the overheated primer. The costly alternative is to remove such primers based on organic binders from the welding area before welding, and preferably also from the reverse side after the welding procedure before application of subsequent coatings, but the additional cost of removing the primer reduces the advantage resulting from high welding speed.

It is also known to use shop primers based on inorganic binders, usually based on silicates. However, these primers contain a large proportion of zinc to ensure the anticorrosive properties, which zinc presents important health risks during the welding operations. Further, MIG/MAG welding of steel covered with primers having a high zinc content results in severe spattering during the welding operations. When making vertical weldings, this spattering is very strongly interfering with the welding process, particularly because the spatters accumulate on the electrode, resulting in short-circuiting and uncontrollability of the weldpool. Since vertical MIG/MAG welding practically has to be carried out semi-automatically, said spattering is also creating unacceptable working conditions for the operator.

There is accordingly a need in the art for providing an improved

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shop primer composition which would allow good weldability in all positions and low spattering, without health hazards and without requiring previous removal of the primer coating from the welding area. Such need particularly exists in the shipbuilding industry, where welding costs represent as much as one fourth of the building costs, in order to take profit of the high speed welding techniques.

An object of the invention is to provide an improved shop primer composition which provides good anti-corrosion properties and good weldability.

Another object of the invention is to provide a shop primer composition which presents acceptable health risks during the welding operations.

A further object of the invention is to provide a shop primer composition which allows welding without requiring previous blasting or grinding of the welding area.

Still another object of the invention is to provide a shop primer whereby no destruction of the primer occurs at the reverse side of the substrate which is welded.

A further object of the invention is to provide a shop primer whereby weld spatters will not adhere to the coated workpiece.

The improved shop primer composition of the present invention comprises :

- (i) fillers and pigments, at least 25 wt % of which have conductive properties;
- (ii) zinc powder, zinc dust or zinc flakes, in a weight ratio of between 1:6 to 1:1 to the total amount of fillers and pigments; said zinc, fillers and pigments being milled to a sufficient fineness;
- (iii) one or more anti-settling agents;
- (iv) optionally, one or more thickening agent;

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(v) a silicate-type binder, in an amount such that the weight ratio of the  $\text{SiO}_2$  content of said binder to the total amount of zinc, fillers and pigments is of from 1:4 to 1:16; and

(vi) one or more solvents.

The Applicant Company has found that, when using shop primer compositions according to the present invention, the coating is compatible with automatic welding techniques in all positions, but also with the other manual welding techniques commonly used in the steel construction industry.

The binder is of the silicate type. Such binders are known in the art, and they comprise the solvent-based alkylsilicate types (with or without terminal silanol groups) and the water-based silicate types, the alkylsilicate binder types being preferred because of better application and recoatability properties.

The alkylsilicate-type binders are produced by high molecular weight condensation of tetraalkylsilicate monomers. Numerous references may be found in the prior art, including (1) U.S. Patent 3,056,684, (2) "The use of ethyl silicate", J.R. Steinmetz, Modern Paint and Coatings, June 1983, and (3) "Filmbildung in anorganischen Zinkstaub-Anstrichen", E.V. Schmid, Farb und Lack, Vol. 84, 1978.

Alkylsilicate-type binders can also be produced as high molecular weight condensate of tetraalkylsilicate monomers without a silanol group at the condensate chain end. References in the prior art include (1) "Single Package Zinc-Rich Coating", T. Ginsberg and L.G. Kaufman, Modern Paint and Coating, October 1981, and (2) "Zinc-Rich Coating Technology" D.M. Berger, G. Associates Ltd., Metal Finishing, March 1975.

Water-based silicate types of binders are usually alkali silicates. Said alkali silicates are also known in the art, as e.g. in

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German Patent 1,669,181 or in "Alkali Silicates in Surface Coatings" (A. Pass and M.J.F. Meason, in "Amalgamated Oxides").

Also known in the art are quaternary ammonium silicate solutions/dispersions in water. These are commercially available, e.g. from Emmery Industries Inc. (Quram Product Line data sheet, June 1980).

The shop primer compositions of the invention are in general prepared as two-component systems, such being more flexible and more economical although it can be envisaged to prepare a one-component system when the silicate binder is based upon an alkylsilicate condensate without a silanol group at the condensate chain end.

The present invention is mainly based upon the particular composition and manufacturing procedure of a special selected pigment mixture of a pigment/filler mixture, e.g. in the form of a paste, which is mixed in certain ratios with a suitable silicate binder, giving dry film properties as hereabove mentioned. While containing good overall properties, and in particular good anti-corrosion properties, the composition of said mixture is characterized by a low zinc content. The composition of the invention will be detailed hereinafter in the particular case of the embodiment wherein a two-component paint is prepared.

The second component is a paste containing fillers, pigments and anti-corrosive agents, together with thickening and anti-settling agents in a solvent mixture. All ingredients should preferably be water-free (max. 0.15 wt % of water), especially when solvent-based silicate binders are used.

Whilst not wishing to be bound by a theory, the paste components may be classified in different types according to their alleged functions.

Zinc powder, zinc dust or zinc flakes are used as anti-corrosive agent, effective because of its galvanic action on the steel substrate.

The pigments or fillers comprise several types. Conductive pigments/



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fillers are an essential part of the composition : they improve both the anti-corrosive properties (by electrically connecting zinc particles with the substrate) and the arc welding properties. Examples of pigments/fillers known to have conductive properties include di-iron phosphide, micaceous iron oxide, derived from natural or synthetic sources, copper flakes, nickel flakes, stainless steel flakes, aluminium flakes dry or as an aluminum flake paste, the micaceous iron oxide types being preferred, resulting in optimal welding and anti-corrosive properties of said invention.

The pigments/fillers used in the composition of the invention may optionally comprise an amount of materials which can interact with the steel substrate, resulting e.g. in some inhibition or passivation of said substrate. This is assumed to slow the consumption of the galvanically active pigment. Examples of pigments/fillers having such properties include chromates like zinc chromate or zinc potassium chromate, phosphates like calcium diphosphate, zinc phosphate, potassium phosphate or sodium potassium polyphosphate, aluminium polyphosphate or borates like zinc metaborate or barium metaborate, and zinc oxide.

Pigments or fillers believed to be inactive are obviously not essential to the invention, although many reasons advocate for their inclusion into the composition, whether for economical reasons, or to provide the primer with a suitable and/or desired colour, or even for improving the coating process (regarding e.g. film-forming, drying or anti-mudcracking properties). As examples of the numerous possible inactive pigments/fillers, it may be cited aluminium silicates, MgAl silicates, barium sulfate, calcium carbonate, titanium dioxide, red iron oxides, yellow iron oxides, chromium oxides, manganese dioxide.

The thickening agent is not essential to the invention. There

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may be used any thickening agent; preferred examples are polyvinyl butyral, melamine formaldehyde, acrylate polymers, nitrocellulose or hydroxyethylcellulose polymers, the latter being preferred. When used, a thickening agent is added in very small amounts, typically of up to 1 wt % relative to the second component.

As anti-settling agent, there may be used any additive like clay-type materials, glycerol trihydroxystearate, polyethylene wax, polyamide-type materials, or their mixtures. The amount used will depend on the anti-settling agent used, and those skilled in the art know that it should not be excessive because this might impart excessive thixotropic properties to the paste. Preferred anti-settling agents are those of the clay type, which are typically added in amounts of from 0.2 to 4 wt % relative to the second component, preferably of from 0.5 to 1.5 wt %.

As solvent for the second component, there is generally used a solvent mixture comprising at least one of the solvents suitable for the first component, and optionally one or several other, less polar, solvents. Examples of such less polar solvents include toluene and xylene. The amount of solvent used will be adjusted by those skilled in the art in relation with the composition of the second component. For practical reasons, it is preferred that the amount of solvents used in both components be such that, when mixed in the desired ratio, the shop primer composition is obtained ready for application; it is further preferred that the composition be adjusted so that the components should be mixed in approximately equal amounts by weight.

The amount of fillers/pigments and anti-corrosive agents in the second component should be such that, after mixing with the first component, the weight ratio of the total of the fillers, pigments and anti-corrosive agents, including any mineral-type anti-settling agent used, to the  $\text{SiO}_2$  content of the silicate binder is of from 4:1 to 16:1,

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preferably of about 17:2.

In addition, the weight ratio of the total amount of anti-corrosive agents to the total amount of fillers and pigments, including any mineral-type anti-settling agent used should be of from 1:6 to 1:1, preferably of from 1:6 to 2:5.

Further, the conductive fillers/pigments should represent at least 25 wt % of the total amount of fillers/pigments.

The hereabove mentioned ratios correspond to a weight ratio of zinc to the total of zinc, fillers, pigments and  $\text{SiO}_2$  of from 4:35 to 16:34, preferably of from 8:63 to 20:63.

It has further been observed that, within the above ranges, the welding properties are improved when the weight ratio zinc:zinc + fillers + pigments +  $\text{SiO}_2$  does not exceed 20:63.

The method for preparing the second component is essential for the invention. In order to obtain minimal spattering during welding and improved anti-corrosive properties, the zinc dust, zinc powder or zinc flakes must be thoroughly grinded, with (depending on their grain size) the conductive pigments and/or residual fillers and/or pigments. The reduction in spattering is obtained by the fact that thorough grinding will prevent agglomerates of zinc dust, zinc powder or zinc flakes to be present in the dried paint film. Zinc particle agglomerates are being thought, besides the zinc concentration, to be the main cause of spattering during welding.

The improved anti-corrosive properties are obtained due to the more effective contact between the optimal dispersed zinc particles and conductive pigments. Improved electrical contact between zinc particles, conductive pigment and the ferrous substrate on which the paint is applied, will eventually lead to optimal usage of the galvanic properties of the

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zinc particles.

In addition, when coarse micaceous iron oxide grades or other coarse conductive pigments are used (fineness above 45 micrometer), thorough grinding is essential to obtain pastes with sufficient fineness. This is necessary to avoid practical problems in case of spray application. Blocking of spray-unit nozzels and excessive wear of spray units are observed in case of using compositions including coarse hard pigments.

Examples of grinding methods are ball milling, and horizontal or vertical grinding with beads, pearls or sand.

For practical reasons, a preferred method uses ball milling during about 24 hours with ceramic balls. It is also possible to use high speed dissolving, but the resulting fineness is usually insufficient. The anti-settling agent is preferably added shortly after milling.

In another embodiment of the invention, the shop primer is prepared as a one-component paint. The binder of a one-component shop primer according to the invention must be a high molecular weight condensate of a tetraalkylsilicate without a terminal silanol group, the alkyl groups being preferably ethyl or propyl groups. The fillers and pigments, and the anti-corrosive and anti-settling agents to be used are as described hereabove, and in the same weight ratios to the binder.

The welding properties obtained with one or two-component shop primers are very similar; a small increase in the corrosion resistance is observed, but this is not sufficient to counterbalance the practical (mostly economical) advantage of two-component paints.

The invention will now be described by reference to the following Examples which are intended to be illustrative and are not intended to limit the scope of the present invention.

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Example 1

## a. Preparation of the first component

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In a stainless steel tank, the following ingredients were introduced at room temperature, while mixing :

- 6 parts by weight (pbw) of isopropylalcohol;
- 19.9 pbw of a prehydrolyzed tetraethylsilicate polymer, having a SiO<sub>2</sub> content of 40 wt %;
- 15.1 pbw of a 1.1 wt % solution of sulphuric acid in a water-2-methoxypropanol mixture (1:4 weight ratio).

The mixture was stirred during two hours, the temperature slowly increasing to a maximum of 35°C. After cooling, there were incorporated a further 57.2 pbw of isopropylalcohol, and 1.8 pbw trimethylborate.

The first component was stored in appropriate plastic cans.

## b. Preparation of the second component

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In a dry tank, the following ingredients were added in the order indicated, and mixed to homogeneity :

- 19.5 pbw of xylene,
- 0.3 pbw of hydroxyethyl cellulose,
- 17.0 pbw of aluminium silicate powder,
- 7.2 pbw of yellow iron oxide powder,
- 17.8 pbw of zinc dust,
- 22.2 pbw of micaceous iron oxide powder,
- 4.0 pbw of an aluminium paste containing 65 wt % of aluminium flakes in white spirit
- 1.6 pbw of 2-methoxypropanol, and
- 4.9 pbw of isopropylalcohol.

The homogeneous mixture was ball milled during 24 hours using

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ceramic balls, when the fineness was measured to be of 0.040 to 0.045mm. The ball mill was rinsed with 4.7 pbw of 2-methoxypropanol and isopropyl alcohol, and 0.8 pbw of bentonite were added before storing the second component into metal cans.

c. Preparation and application of the shop primer  
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The two components were mixed in a 1:1 weight ratio. The shop primer was applied with an air spray, so as to form a 0.025 mm thick layer after drying.

d. Evaluation of the porosity obtained when welding over the shop primer layer  
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The specifications DVS-0501 (Deutscher Verband für Schweißtechnik, Postfach 2726, Aachenerstrasse 172, D-4000 Düsseldorf) were followed throughout, except as mentioned hereunder.

The metal welding was carried out under a gas mixture containing 80% argon and 20% carbon dioxide, with automatic feeding of the electrode. The electrodes used were 1.2 mm diameter CORE WELD 70 NI metal filled electrodes. The welding conditions were as follows :

- welding speed : 30 cm/min.
- gas flow : 15 l/min.
- continuous current : 30 V, 200 A
- weldseam thickness : 4 mm

After welding, the external porosity was examined visually. The weld was then broken, while brought at a temperature of about 200°C, to examine the internal porosity.

For comparative purposes, the same evaluation tests were carried out with two commercial shop primers, also based on alkyl silicates but containing as much as about 70 wt. % of zinc in the dry film. These

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commercial primers will be designated as A and B.

The visual examination of the external porosity over a length of 10 cm of the weldseam showed 4 holes with the primer of the invention, 5 holes with primer A and 6 holes with Primer B.

The results of the internal porosity determination were as follows :

this invention : 24 holes/10 cm; total section area : 5.6 mm<sup>2</sup>  
primer A : 55 holes/10 cm; total section area : 13.1 mm<sup>2</sup>  
primer B : 47 holes/10 cm; total section area : 10.8 mm<sup>2</sup>

#### Example 2

a) Preparation of the first component : see example 1

b) Preparation of the second component

The composition used was identical to the second composition described in Example 1, however the inactive fillers were not included in the ball mill procedure because they already had a sufficiently fine grain size. This resulted in a more efficient and economical manufacturing procedure without noticeable influence on welding and anti-corrosive properties.

In a dry tank the following ingredients were added in the order indicated and mixed to homogeneity :

19.5 pbw of xylene

0.3 pbw of hydroxyethylcellulose

22.2 pbw of micaceous iron oxide powder (coarse grade)

17.8 pbw of zinc dust

4.0 pbw of aluminium paste containing 65 wt % of aluminium flakes in white spirit.

The homogeneous mixture was ball milled during 24 hours using

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ceramic balls when the fineness was measured to be of 0.040 to 0.045 mm. The ball mill was rinsed with 4.7 pbw of 2-methoxy-propanol and isopropylalcohol.

The raw materials not requiring ball milling were added together with the bentonite and dispersed to fineness with a high speed dissolver.

17.0 pbw of aluminium silicate powder

7.2 pbw of yellow iron oxide powder

0.8 pbw of bentonite

1.6 pbw of 2-methoxy-propanol

4.9 pbw of isopropylalcohol

c) Preparation and application of shop primer

See example 1 item c

### Example 3

a) Preparation of the first component : see example 1.

b) Preparation of the second component.

The composition used was identical to the second composition described in example 2, however the inactive filler (aluminium silicate powder) is replaced by the active filler zinc oxide. This replacement resulted in improved anti-corrosive properties with respect to examples 1 and 2, without noticeable influence on weldability.

In a dry tank the following ingredients were added in the order indicated and mixed to homogeneity.

19.5 pbw of xylene

0.3 pbw of hydroxyethylcellulose

17.8 pbw of zinc dust



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22.2 pbw of micaceous iron oxide powder (coarse grade)

4.0 pbw of aluminium paste containing 65 wt % of aluminium flakes in white spirit

3.0 pbw of isopropylalcohol

The homogeneous mixture was ball milled during 24 hours using ceramic balls when the fineness was measured to be of 0.040 to 0.045 mm. The ball mill was rinsed with 4.7 pbw of 2-methoxy propanol and isopropylalcohol. The new materials not essential to be ball milled were added together with the bentonite and dispersed to fineness with a high speed dissolver.

14.0 pbw of zinc oxide (lead free grade)

3.0 pbw of aluminium silicate powder

7.2 pbw of yellow iron oxide powder

0.8 pbw of bentonite

1.6 pbw of 2-methoxypropanol

1.9 pbw of isopropylalcohol

c) Preparation and application of shop primer

See example 1.

#### Example 4

a) Preparation of first component

See example 1

b) Preparation of second component

The composition was identical to the second composition described in example 2, however 6.1 pbw of the inactive filler aluminium silicate powder was replaced by barium metaborate commercially available as Butrol 11 MI supplied by Buckman Laboratories S.A. This replacement resulted in

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improved anti-corrosive properties with respect to examples 1 and 2, however having slight adverse effects on weldability.

c) Preparation and application of shop primer.

See example 1.

#### Example 5

a) Preparation of first component.

See example 1.

b) Preparation of second component.

The composition used was identical to the second composition described in Example 2. However 15.7 pbw of the inactive filler aluminium silicate powder was replaced by aluminium polyphosphate commercially available as K-white 84 supplied by Teikoku Kako Co Ltd. This replacement resulted in slightly improved anti-corrosive properties with respect to examples 1 and 2, however having no noticeable effects on weldability.

c) Preparation and application of shop primer

See example 1

#### Example 6

a) Preparation of first component.

See example 1.

b) Preparation of second component

The composition used was identical to the second composition described in Example 2, however instead of zinc dust, zinc flakes commercially available as zinc powder ECKA NP 31129/G supplied by Eckhart-Werke were used. This replacement resulted in slightly

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improved anti-corrosive properties with respect to Examples 1 and 2, however having no noticeable effects on weldability.

c) Preparation and application of shop primer

See example 1

#### Example 7

a) Preparation of first component

See example 1.

b) Preparation of second component

The composition used was identical to the second composition described in Example 2; however instead of the coarse micaceous iron oxide powder derived from natural sources, synthetic micaceous iron oxide powder of a fine grade (average fineness < 0.030 mm), commercially available as Laminox F supplied by MPLC Laboratories Limited was used.

Due to the fine grade, there was no need anymore to ball mill the micaceous iron oxide together with the zinc particles, and it was added after the ball mill procedure together with the inactive or active fillers and pigments.

c) Preparation and application of shop primer.

See example 1.

#### Example 8

a) Preparation of first component

See example 1.

b) Preparation of second component

In this composition the amount of zinc was increased.

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In addition, the active filler zinc oxide was used instead of the inactive aluminium silicate powder. The composition was formulated to obtain long time anti-corrosive properties at reduced dry film thickness.

In a dry tank the following ingredients were added in the order indicated and mixed to homogeneity :

19.5 pbw of xylene

0.3 pbw of hydroxyethyl cellulose

32.7 pbw of zinc dust

20.5 pbw of micaceous iron oxide powder (coarse grade)

4.0 pbw of aluminium paste containing 65 wt % of aluminium flakes in white spirit

2.3 pbw of isopropylalcohol

The homogeneous mixture was ball milled during 24 hours using ceramic balls when the fineness was measured to be of 0.040 mm to 0.045 mm. The ball mill was rinsed with 4.4 pbw of 2-methoxy propanol and isopropanol. The raw materials not essential to be ball milled were added together with the bentonite and dispersed to fineness with a high speed dissolver :

6.7 pbw if zinc oxide (lead free grade)

7.2 pbw of yellow iron oxide powder

0.8 pbw of bentonite

1.6 pbw of 2-methoxypropanol

c) Preparation and application of shop primer

See example 1, however the applied dry film thickness was 0.015 mm.

#### Example 9 (comparative)

a) Preparation of first component

See example 1.

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## b) Preparation of second component

The composition used was identical to the second composition described in Example 2, however the zinc dust was not ball milled but added together with inactive fillers and pigments. This example is meant to be illustrative showing that milling the zinc dust, zinc powder or zinc flakes to a sufficient fineness is essential to obtain improved weldability and anti-corrosive properties.

## c) Preparation and application of shop primer

See example 1

Example 10

In a dry tank, the following ingredients were added in the order indicated and mixed to homogeneity :

- 9.05 pbw of xylene,
- 1.15 pbw of polyvinylbutyral,
- 6.9 pbw of quartz powder,
- 3.7 pbw of yellow iron oxide powder,
- 8.55 pbw of zinc dust,
- 14.45 pbw of di-iron phosphide,
- 0.8 pbw of xylene, and
- 5.2 pbw of isopropyl alcohol.

The homogeneous mixture was ball milled during 24 hours, using ceramic balls. The fineness of the resulting mixture was measured to be of about 0.040 mm to 0.045 mm.

After transferring to a tank, the mill was rinsed with 33.3 pbw of toluene which were also transferred to said tank.

The following ingredients were then added and mixed to

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homogeneity :

0.5 pbw of bentonite,

15.7 pbw of a silicate binder, without terminal silanol group at the condensate chain end, containing 35 wt % of  $\text{SiO}_2$ ; and

0.7 pbw of triethanolamine.

The resulting one-component primer composition was stored in metal cans, ready for application (except for viscosity adjustments).

The primer was applied on shotblasted steel panels, as per example 1, item c.

Evaluation of the MIG/MAG welding results of examples 1-10

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#### Experimental

In each experiment two panels were put together to form a T-joint and welded on both faces, called the leading (first) side and the trailing (second) side. The MIG/MAG welding experiments were carried out for two positions, the 2F-position and the 3F-position. The welding in the horizontal 2F-position was carried out fully automatic. The torch was transported alongside the T-joint side by an apparatus known as "tracker". The welding in the vertical 3F-position was carried out downwards, manually (semi-automatic MIG/MAG welding).

#### General information

MIG welding apparatus : ESAB LAH 500

wire unit : ESAB A 10 MEC 44

Shielding gas : 80% Argon, 20%  $\text{CO}_2$

(commercial name AGAmix 20, supplied by AGA gas - Holland)

Flow : 15 l/min.

Welding plates : shotblasted steel

size 400 x 120 x 10 mm

2F-position (see table 1)

Welding speed : 40-60 cm/min.

Welding current : 280-320 A

Welding voltage : 32 V

Wire type : solid wire, SG2 (DIN 8555)

diameter 1.2 mm

3F-position - Downwards (see table 2)

Welding speed : 30-60 cm/min.

Welding current : 200-220 A

Welding voltage : 2.7 V

Wire type : solid wire, SG2 (DIN 8555)

diameter 1.0 mm

Table 1 : Results of MIG/MAG welding on the 2F-welding position

Example N°	Arc Stability	Amount of Spattering (1)	Visual porosity		Buried porosity	
			Leading	Trailing (2)	Leading	Trailing (2)
1	good	2	none	none	none	<5%
2	good	2	none	none	none	<5%
3	good	2	none	none	none	<5%
4	reasonable	5	none	3 pores	10-15%	15-20%
5	good	2	none	none	none	<5%
6	good	2	none	none	none	5-10%
7	good	2	none	none	none	<5%
8	reasonable	3	none	none	none	5%
9	unstable	5	none	none	none	15-20%
10	good	2	none	none	none	<5%

Remarks

(1) scale 0-10

0 means : amount of spattering as observed when MIG/MAG welding  
shotblasted steel under identical conditions

10 means : excessive spattering, no welding possible

(2) the percentage is the ratio :  $\frac{\text{pore area}}{\text{total weldseam area}} \times 100$



Table 2 : Results of MIG/MAG welding in 3F-downwards position

Example N°	Arc Stability	Amount of Spattering (1)	Visual porosity		Buried porosity	
			Leading	Trailing (2)	Leading	Trailing (2)
1	good	2	none	none	none	<5%
2	good	2	none	none	none	<5%
3	good	2	none	none	none	<5%
4	reasonable	5	none	2 pores	10-15%	15-20%
5	good	2	none	none	none	<5%
6	good	2	none	none	none	<5%
7	good	2	none	none	none	<5%
8	reasonable	3	none	none	none	5-10%
9	unstable	7	1 pore	5 pores	<5%	15-20%
10	good	2	none	none	none	<5%

Remarks : (1) and (2) see table 1.

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Outdoor weathering test according to ASTM D 1104 specification.

The test panels (150 x 150 x 10 mm) were shotblasted to an average roughness of 0.045 mm. The primer was applied on a dry film thickness per item 1.c of previous described examples. The coated panels were exposed outdoor at 45° facing south, according to ASTM D 1104, at location Uithoorn, the Netherlands. After 2 months exposure, the corrosion was estimated according the rustscale disclosed on ASTM D 610 (see table 3).

Table 3 : results of outdoor exposure according to ASTM D 1104 specification

Example n°	Rust grade (ASTM D 610)
1	7
2	7
3	9-10
4	8-9
5	8
6	7-8
7	6-7
8	9-10
9	2
10	7-8

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Claims

1. Shop primer composition comprising
  - (i) fillers and pigments, at least 25 wt % of which have conductive properties;
  - (ii) zinc powder or zinc dust, in a weight ratio of between 1:6 to 1:1 to the total amount of fillers and pigments;  
said zinc, fillers and pigments being milled to a sufficient fineness;
  - (iii) one or more anti-settling agents;
  - (iv) optionally, one or more thickening agent;
  - (v) a silicate-type binder, in an amount such that the weight ratio of the SiO<sub>2</sub> content of said binder to the total amount of zinc, fillers and pigments is of from 1:4 to 1:16; and
  - (vi) one or more solvents.
2. Shop-primer according to claim 1, wherein the silicate-type binder is dissolved in part of the solvents and stored separately.
3. Shop primer according to either of Claims 1 or 2, wherein the silicate-type binder is of the alkylsilicate type having no silanol group at the condensate chain end.
4. Shop primer according to Claim 2, wherein the silicate-type binder is selected from the group comprising the alkali silicate type, and the quaternary ammonium silicate type.
5. Shop primer according to Claim 2, wherein the silicate-type binder is of the alkylsilicate type having silanol groups at the condensate chain end.
6. Shop primer according to any one of Claims 1 to 5, wherein the weight ratio of the zinc to the fillers and pigments is of from 1/6 to 2:5.
7. Shop primer according to any one of Claims 1 to 6, wherein the weight ratio of the zinc, fillers and pigments to the SiO<sub>2</sub> of the binder is of

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about 8:1.

8. Shop primer according to any one of Claims 1 to 7, wherein the weight ratio of the zinc to the total of the zinc, fillers, pigments and  $\text{SiO}_2$  of the binder does not exceed 20:63.

# INTERNATIONAL SEARCH REPORT

International Application No PCT/BE 88/00003

<b>I. CLASSIFICATION F SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup> According to International Patent Classification (IPC) or to both National Classification and IPC IPC <sup>4</sup> :      C 09 D 5/10																				
<b>II. FIELDS SEARCHED</b> <div style="text-align: right; margin-right: 100px;">Minimum Documentation Searched <sup>7</sup></div> <table style="width: 100%; border: none;"> <tr> <td style="width: 30%; border: none;">Classification System</td> <td style="border: none;">Classification Symbols</td> </tr> <tr> <td style="border: none; padding-top: 10px;">IPC<sup>4</sup></td> <td style="border: none; padding-top: 10px; text-align: center;">C 09 D</td> </tr> </table> <div style="text-align: center; margin-top: 10px; font-size: small;">         Documentation Searched other than Minimum Documentation          to the Extent that such Documents are Included in the Fields Searched <sup>8</sup> </div>			Classification System	Classification Symbols	IPC <sup>4</sup>	C 09 D														
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<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%; text-align: left; font-size: small;">Category <sup>10</sup></th> <th style="width: 70%; text-align: left; font-size: small;">Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup></th> <th style="width: 20%; text-align: left; font-size: small;">Relevant to Claim No. <sup>13</sup></th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td>US, A, 4086096 (G.D. McLEOD) 25 April 1978 see column 3, lines 51-61; claims 1,2 --</td> <td style="text-align: center; vertical-align: top;">1</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>DE, A, 2460546 (DAINIPPON TORYO K.K.) 12 February 1976 see page 4, lines 3-9; examples; claim 1 --</td> <td style="text-align: center; vertical-align: top;">1</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>EP, A, 0064344 (MOBIL OIL CORP.) 10 November 1982 see page 4, lines 26-32; page 5, lines 18,20; page 8, line 17; page 9, lines 29-31; pages 14-15 --</td> <td style="text-align: center; vertical-align: top;">1</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>US, A, 3888575 (M. FUJII et al.) 10 June 1975 --</td> <td style="text-align: center; vertical-align: top;">1</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>DE, A, 2711896 (STAUFFER CHEMICAL) 21 September 1978 -----</td> <td style="text-align: center; vertical-align: top;">1</td> </tr> </tbody> </table>			Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>	X	US, A, 4086096 (G.D. McLEOD) 25 April 1978 see column 3, lines 51-61; claims 1,2 --	1	Y	DE, A, 2460546 (DAINIPPON TORYO K.K.) 12 February 1976 see page 4, lines 3-9; examples; claim 1 --	1	Y	EP, A, 0064344 (MOBIL OIL CORP.) 10 November 1982 see page 4, lines 26-32; page 5, lines 18,20; page 8, line 17; page 9, lines 29-31; pages 14-15 --	1	A	US, A, 3888575 (M. FUJII et al.) 10 June 1975 --	1	A	DE, A, 2711896 (STAUFFER CHEMICAL) 21 September 1978 -----	1
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<div style="display: flex; justify-content: space-between; font-size: x-small;"> <div style="width: 45%;"> <p>* Special categories of cited documents: <sup>14</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 50%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p> </div> </div>																				
<b>IV. CERTIFICATION</b> <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none; vertical-align: top;">           Date of the Actual Completion of the International Search             25th April 1988         </td> <td style="width: 50%; border: none; vertical-align: top;">           Date of Mailing of this International Search Report   <div style="text-align: right; font-size: large; font-weight: bold;">09 JUN 1988</div> </td> </tr> <tr> <td style="border: none; vertical-align: top;">           International Searching Authority             EUROPEAN PATENT OFFICE         </td> <td style="border: none; vertical-align: top;">           Signature of Authorized Officer  <div style="text-align: right; font-weight: bold;">P.E.G. VAN DER PUTTEN</div> </td> </tr> </table>			Date of the Actual Completion of the International Search  25th April 1988	Date of Mailing of this International Search Report  <div style="text-align: right; font-size: large; font-weight: bold;">09 JUN 1988</div>	International Searching Authority  EUROPEAN PATENT OFFICE	Signature of Authorized Officer <div style="text-align: right; font-weight: bold;">P.E.G. VAN DER PUTTEN</div>														
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# ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

BE 8800003

SA 21238

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4086096	25-04-78	None	
DE-A- 2460546	12-02-76	GB-A- 1459574	22-12-76
		US-A- 4011088	08-03-77
		JP-A- 51020230	18-02-76
EP-A- 0064344	10-11-82	JP-A- 57182363	10-11-82
		AU-A- 8227782	28-10-82
US-A- 3888575	10-06-75	None	
DE-A- 2711896	21-09-78	None	

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